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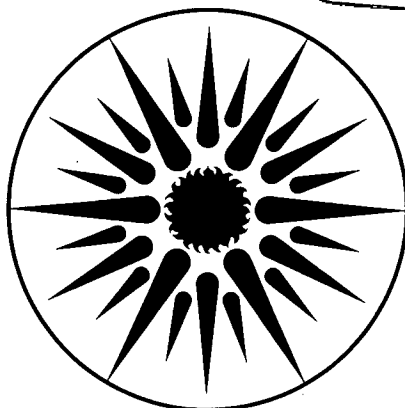
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OF AMMONIA FROM SOUR WATER

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In many industrial applications, volatile weak acids, such as CO_2 and H_2S, and weak bases, such as NH_3, are present in significant quantities in wastewaters. Condensate waters from coal-conversion processes contain all three of these components at a pH around 8.5 to 9. Refinery sour waters typically contain NH_3 and H_2S at pH about 7.5. Energy requirements for removing these contaminants by ordinary steam stripping can be large, requiring a boil-up of 10 to 20% of the feed water (1). Isolating individual components in order to sell the ammonia and/or to send the H_2S to a Claus plant is even more energy intensive. For example, the Phosam-W and the all-distillation processes require a boil-up of about 25 to 30% of the feed water (2). These high steam requirements result from the interaction between the acidic and basic components, suppressing the volatilities. At the pH of these waste-waters, NH_3, CO_2 and H_2S are largely ionized. Only the unionized form is volatile, so the presence of the base serves to decrease the volatility of the acid and vice versa.

Cahn et al.(3) have proposed combining two separation processes to remove ammonia and acid gases from wastewaters more effectively. They suggest using liquid-membrane extraction to remove ammonia and simultaneous steam stripping to remove the acid gases--a combined process which they call extripping. This combination overcomes the self-limiting factors of either process alone. Stripping the acid gases from solution raises the pH, increasing the permeability of the ammonia through the liquid membrane. Removing the NH_3 by permeation lowers the pH, increasing the volatility of the acid gases. These combined effects can lower steam requirements. In addition, both this process and the one suggested below have the advantage of isolating the NH_3 from the acid gases. However, if a strong acid is used as the inner phase in liquid-membrane extraction of NH_3, there is no easy way to convert the salt back to NH_3.

In the present work, the possibility of combining solvent extraction with simultaneous steam stripping is investigated. A primary goal is to define a suitable solvent for the process that [1] has a high capacity and selectivity for either the basic or the acidic components, [2] results in low solvent losses to the aqueous phase through solubility losses and/or incomplete phase separation, [3] is easily regenerable by stripping or distillation at a temperature above that of the original extraction, [4] has a reasonable viscosity and density, and [5] is inexpensive and readily available.

SOLVENT SELECTION

No common solvents were found to be effective for extraction of either CO_2 or H_2S (4). Attempts to remove ammonia from an aqueous ammonium bicarbonate solution with neodecanoic acid (Exxon Chemical Co.), 2-ethylhexanoic acid, octanol, 50% decanol in toluene, toluene or methyl isobutyl ketone (MIBK) also met with failure.

These results reveal the need to extract the ionic form of the desired species, rather than relying on the physical solubilities of the gases in an organic solvent. Therefore, liquid cation exchangers were tested as possible extractants for ammonia. These compounds exchange their hydrogen ions for ammonium ions at the aqueous/organic interface. The equilibrium becomes more favorable at higher pH, up until the point where competition from another ion used to raise the pH becomes important. The liquid cation exchangers tested — dinonylnaphthalene sulfonic acid (DNNSA), octylphenyl phosphoric acid (OPAP), and di-2-ethylhexyl phosphoric acid (D2EHPA) — all readily extract ammonia, typically exhibiting an equilibrium distribution coefficient (weight-fraction basis) for NH_3 substantially greater than unity(4). OPAP, a stronger acid than D2EHPA, was found to be more water soluble than D2EHPA. DNNSA, also a stronger acid than D2EHPA and therefore a stronger extractant, could not be regenerated by stripping at elevated temperatures. No ammonia was stripped from the loaded solvent at temperatures less than 150°C, and above about that temperature a solid precipitated out of the solvent. Analysis of the solid showed that it contained nitrogen in addition to carbon, hydrogen, oxygen and sulfur. This indicated that ammonia was incorporated into the thermal degradation product of DNNSA. In light of these results, D2EHPA was the extractant chosen for further analysis.

D2EHPA, commonly used in the hydrometallurgical industry, is a viscous liquid with a density of 0.973 g/ml. Therefore, to achieve desirable physical properties, it is necessary to mix D2EHPA with a less viscous, lower-density diluent. In addition, several other difficulties can arise in the use of liquid ion exchangers such as D2EHPA. Since they are ionic, they tend to be surface active and significantly soluble in the aqueous phase, particularly in the salt form. This can result in poor phase separation and excessive extractant losses. The choice of organic diluent can greatly influence these properties, as well as the capacity of the extractant for ammonia and its regenerability.

CAPACITY FOR AMMONIA AND EXTRACTANT LOSSES

Capacity for ammonia and extractant losses were quantified as follows: A solution of 0.2M D2EHPA in a given diluent was contacted with an aqueous

ammonium bicarbonate solution containing 0.58$\underline{M}$ ammonia in a single batch-equilibrium contacting at an aqueous-to-organic phase ratio of 0.185. The pH of the feed aqueous solution was about 8. The ammonia concentrations in the feed and the raffinate were measured with a specific-ion electrode (Orion Corp., Model 951000). The concentration of phosphorus-containing compounds in the raffinate was measured by a standard decomposition and preciptation method(5). All D2EHPA used was first purified by the copper-salt-precipitation method (6).

A diluent which associates preferentially with D2EHPA on a molecular level will lower the activity of D2EHPA and thus decrease its ability to extract ammonia. However, if the diluent interacts more strongly with the ammonia-D2EHPA complex than with the D2EHPA itself, a higher percent extraction of ammonia results. Lowering the activity of either D2EHPA or its ammonium salt can also lead to lower extractant losses through aqueous solubility.

The degree of ammonia extraction by D2EHPA is greater in the presence of an inert diluent, such as an aliphatic hydrocarbon, than in the presence of an aromatic, such as toluene. This is probably due to the interaction of the π electrons of the aromatic with D2EHPA, which reduces the availability of D2EHPA for extraction of ammonia. Under identical conditions, using Norpar 12 (C_{11} to C_{13} paraffins, King Industries) as diluent, 96% of the ammonia is extracted from an aqueous solution, while only 94% is extracted when the diluent is toluene. Likewise, replacing an aliphatic diluent with an aromatic reduces extractant losses by about 50%, because the aromatic can solvate the D2EHPA and its ammonium salt better than the aliphatic can.

Using a mixed diluent of toluene plus a modifier with D2EHPA takes advantage of the chemical nature of a modifier which might be too viscous to be

used alone. Several Lewis acids and bases added as modifiers to toluene in a mixed diluent were examined for their effects on the capacity of D2EHPA for ammonia and on extractant losses to the aqueous phase. Figures 1 and 2 summarize the data.

The bases tested, in order of decreasing ability to donate electrons, were Amberlite LA-2 (secondary amine, Rohm and Haas), Adogen 364 (tertiary amine, Sherex Div. Ashland Chemicals), TOPO (trioctylphosphine oxide, American Cyanamid Corp.), isobutyl heptyl ketone (IBHK), and n-hexyl ether. The strongest bases appear to interact to the greatest extent with D2EHPA and dramatically decrease both the degree of ammonia extraction and the aqueous extractant loss (Figure 1). These effects lessen as base strength decreases. In fact, the two weakest bases tested have little effect on ammonia extractability and actually increase extractant losses. 1,1,2,2-Tetrachloroethane, a Lewis acid, increases aqueous extractant losses to a still greater extent. On the other hand, the use of carboxylic acids, especially straight-chain ones such as 1-decanoic acid, as modifiers with D2EHPA and toluene greatly enhances the extraction of ammonia (Figure 2), although these acids themselves do not have a high capacity ammonia. Extractant losses are significantly decreased by the addition of these acids. Sterically unhindered alcohols, such as n-decanol and n-octanol, and phenols, such as 2,4-dimethyl phenol and nonyl phenol, behave similarly. More hindered compounds, such as neodecanoic acid, 2-ethyl-1-hexanol and 4-sec-butyl-2(α-methylbenzyl) phenol, do not exhibit this same degree of enhancement. Apparently, only compounds with available -OH groups can solvate both D2EHPA and its ammonium salt to the extent necessary to reduce extractant losses yet maintain reasonable D2EHPA capacity for ammonia.

To simulate extractant losses in an aqueous stream leaving a stripper, raffinates from a batch extraction were extracted a second time with fresh organic. For a 50% decanol-in-toluene (v/v) diluent, aqueous D2EHPA1 losses were reduced to 84 ppm by the second extraction. At a D2EHPA cost of $5.95 per kg., this loss corresponds to $0.50 (U.S.) per m^3 of water treated. For a 6.5% decanol-in-toluene (v/v) solution as diluent, losses after the second extraction were 116 ppm, corresponding to $0.69 (U.S.) per m^3 of water treated.

PHASE SEPARATION

Poor phase separation in these systems manifests itself as a white emulsion at the interface. In order to improve the phase separation, attempts were made to reduce the surfactant nature of the system. The ammonium salt of D2EHPA is highly surface active, and so it was found that operating under conditions such that there was low conversion of the D2EHPA to the salt form improved the phase separation. Modifiers that interact with the ammonium salt of D2EHPA can decrease its interfacial activity and thereby improve phase separation. Hence, the sterically unhindered carboxylic acids, alcohols and phenols added as modifiers to toluene greatly improve phase separation, particularly at high modifier concentrations. Likewise the modifiers IBHK and n-hexyl ether, which do not interact strongly with the ammonia-D2EHPA complex, have poor separation properties. Other factors which appear to result in poor phase separation are certain combinations of low raffinate concentrations, high initial concentrations of D2EHPA in the organic phase, and low solvent-to-water ratios, which indicate a tendency to form oil-in-water emulsions.

REGENERATION

The above results lead to the choice of 50% decanol in either an aromatic or aliphatic as a suitable diluent for D2EHPA. Attempts to regenerate a solution containing 0.2M D2EHPA in a diluent composed of 50% isodecanol in Chevron Solvent No. 25 (mixed alkylbenzenes, Chevron Chemical Co.), loaded to 0.1M NH_3, by stripping at 165°C for four hours, led to significant decomposition of the D2EHPA (4). Regeneration of a similar solvent at 110°C for seven hours yielded no signs of thermal decomposition of the solvent. Decomposition of the solvent was qualitatively monitored through color change of the solvent and through a comparison of D2EHPA aqueous extractant losses from the regenerated solvent and from fresh solvent in two successive batch extractions, as described above.

Quantitative data for the partial pressure of ammonia above an organic solvent that is 0.48M D2EHPA in 50% isodecanol/Norpar 12, originally loaded to 0.47M NH_3, indicate that NH_3 has less than one-tenth the volatility needed for convenient regeneration by stripping at atmospheric pressure and 100°C. Further regeneration studies are needed, either at higher temperatures (but probably less than 165°C), or with an inhibitor that is effective against D2EHPA decomposition, or with a diluent that has a lower extraction efficiency for ammonia, corresponding to the ammonia being not as tightly held and therefore more readily liberated from the solvent. A trade-off may exist here between costs for extractant losses, through either aqueous solubility or thermal decomposition, and steam requirements for regeneration.

STRIPPING VS. EXTRIPPING

Figure 3 compares results for batch stripping and batch extripping processes. In both experiments, 50 mL of an aqueous solution containing 0.6M CO_2 and 0.56M NH_3 were stripped with nitrogen at room temperature. In the extripping experiment an organic solvent containing 0.2M D2EHPA in Norpar 12 was also present, at a solvent-to-water ratio of 5. A comparison of the two experiments shows that the CO_2 volatility is greatly increased in the extripping case, as indicated by its much more rapid removal from solution. Further, in the extripping case 93% of the ammonia was extracted into the organic phase, while less than 0.5% of it was stripped from solution. These are precisely the characteristics desired - an enhancement in CO_2 volatility and an isolation of the NH_3 from the CO_2.

CONCLUSIONS

1. Liquid cation exchangers extract ammonia effectively from aqueous ammonium bicarbonate solutions.

2. D2EHPA is an effective extractant for ammonia.

3. Compounds with available - OH groups are desirable modifiers to add to the diluent for D2EHPA, subject to the need for sustaining sufficient NH_3 volatility for regeneration.

4. Simultaneous stripping and selective solvent extraction of an aqueous solution of NH_3 and CO_2 does produce the desired results of enhanced CO_2 volatility and isolation of NH_3 from CO_2.

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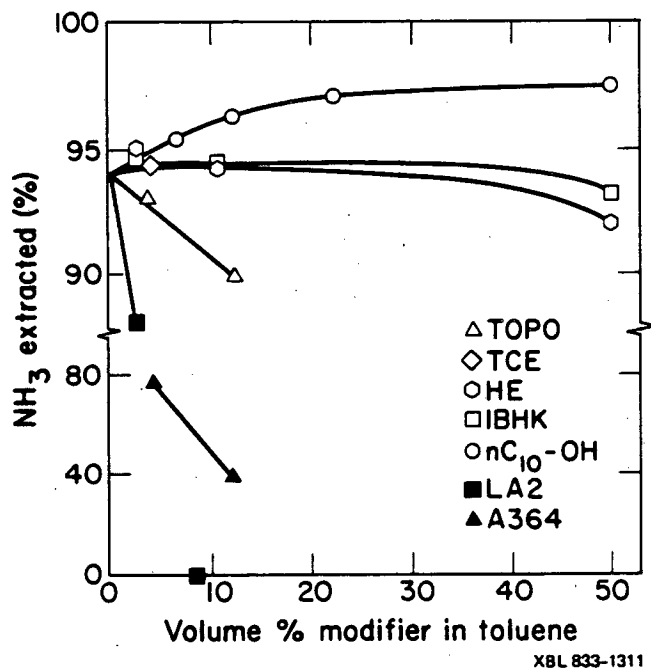## REFERENCES

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Figure 1. EFFECTS OF VARIOUS LEWIS ACIDS AND BASES AS MODIFIERS MIXED WITH TOLUENE AS DILUENTS FOR D2EHPA.

(Aqueous Feed = 0.58 $\underline{M}$ NH_4HCO_3; 0.2 $\underline{M}$ D2EHPA in Organic Phase; Organic/Aqueous Phase Ratio = 5/1, v/$\overline{v}$. Modifiers: TOPO = Trioctylphosphine oxide; TCE = 1,1,2,2-Tetrachloroethane; HE = n-hexyl ether; IBHK = isobutyl heptyl ketone; nC_{10}-OH = n-decanol; LA2 = Amberlite LA2; A364 = Adogen 364).
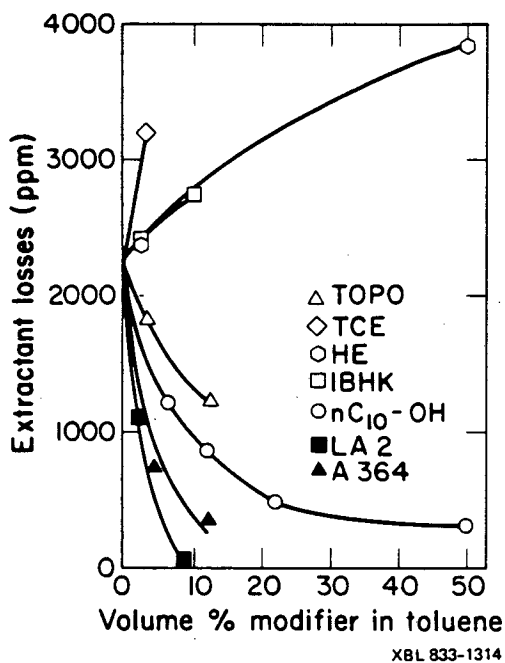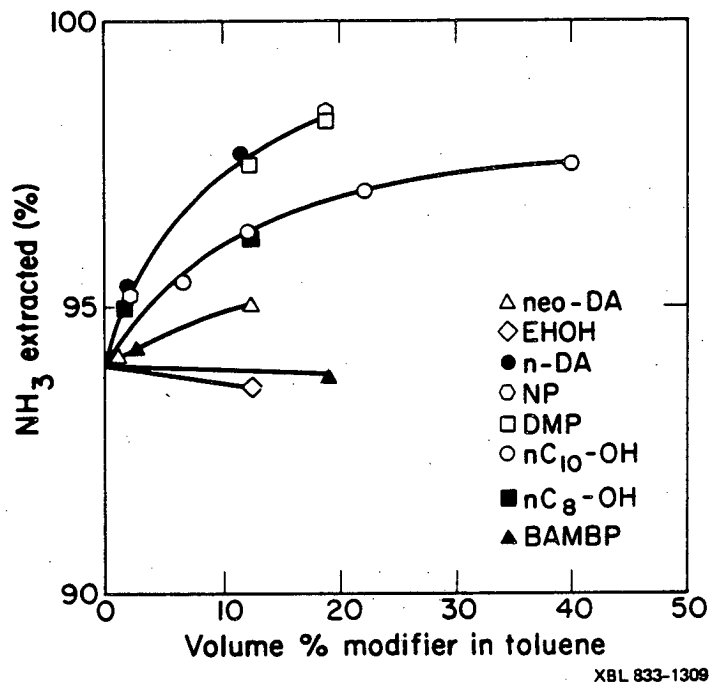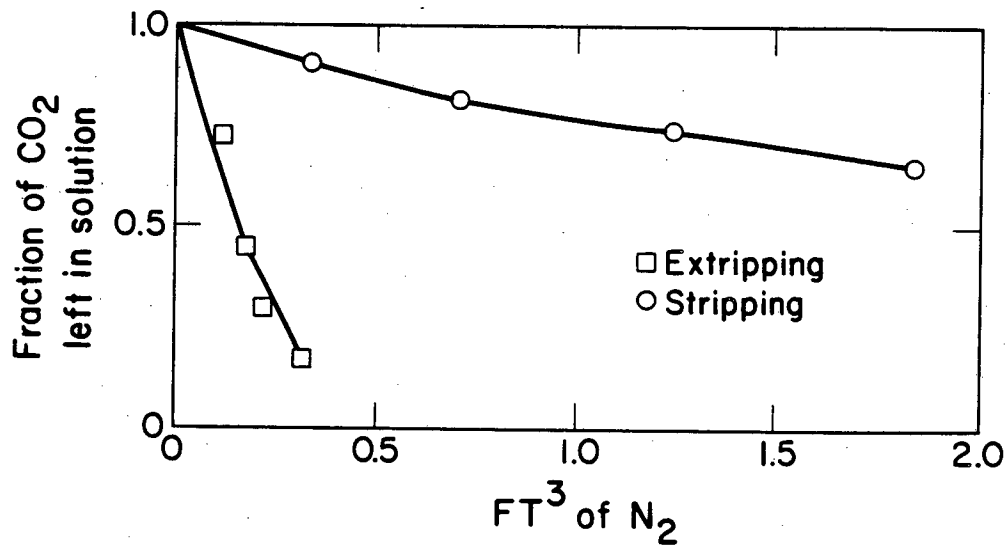

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a. Effects of Modifiers on Extraction of Ammonia.

XBL 833-1314

b. Effects of Modifiers on Phosphorus Content of Aqueous Phase, expressed as ppm D2EHPA.

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Figure 2. EFFECTS OF VARIOUS ALCOHOLS, ACIDS AND PHENOLS AS MODIFIERS MIXED WITH TOLUENE AS DILUENTS FOR D2EHPA.

(Aqueous Feed = 0.58 $\underline{M}$ NH_4HCO_3; 0.2 $\underline{M}$ D2EHPA in Organic Phase; Organic/Aqueous Phase Ratio = 5/1 v/v. Modifiers: neo-DA = neodecanoic acid; EHOH = 2-ethyl-1-hexanol; n-DA = n-decanoic acid; NP = nonyl phenol; DMP = 2,4-dimethyl phenol; nC_{10}-OH = n-decanol; nC_8-OH = n-octanol; BAMBP = 4-sec-butyl-2-(α-methyl benzyl)phenol).

a. Effects of Modifiers on Extraction of Ammonia.
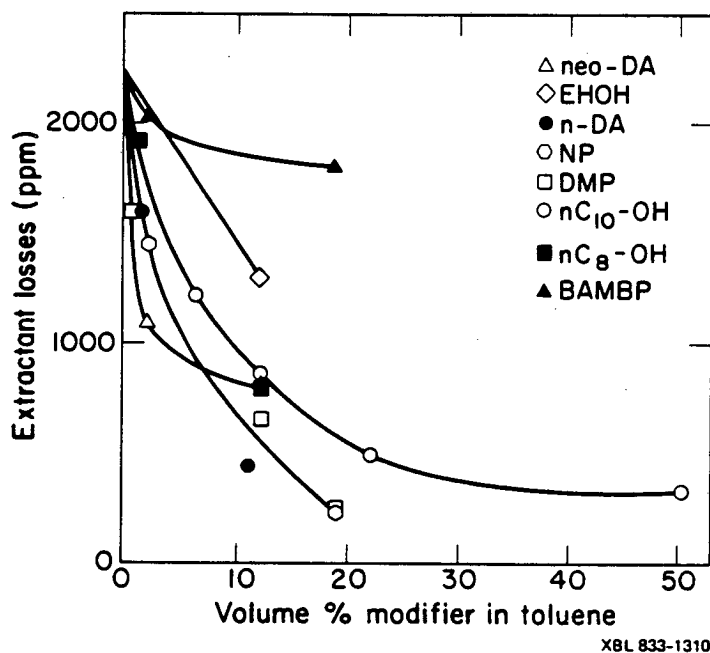
b. Effects of Modifiers on Phosphorus Content of Aqueous Phase, expressed as ppm D2EHPA.

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Figure 3. COMPARISON OF RATE OF REMOVAL OF CO_2 BY STRIPPING WITH THAT BY EXTRIPPING.

(Stripping: Aqueous Feed = 50 ml of 0.6 $\underline{M}$ CO_2, 0.56 $\underline{M}$ NH_3. Extripping: Aqueous Feed = same; Organic Phase = 0.2 $\underline{M}$ D2EHPA in Norpar 12; Organic/Aqueous Phase Ratio = 5/1, v/v).

XBL 833-1313